controlled free radical, metathesis ring opening and coordination polymerization.

70. The initiator of Claim 69 wherein said non-ATRP polymerization is a cationic or ring opening polymerization.

71. The initiator of Claim 69 wherein said non-ATRP polymerization is an anionic polymerization.

72. The initiator of Claim 69 wherein said non-ATRP polymerization is a free radical polymerization.

73. A macroinitiator for the preparation of block copolymers, comprising the initiator of Claim 69.

74. A process for the preparation of block copolymers from free radically (co)polymerizable monomers comprising initiating a first temperature ATRP process with the initiator of Claim 72 to form a macroinitiator for a second temperature free radical polymerization, wherein said first temperature is lower than said second temperature, and wherein said initiator of Claim 72 comprises a first group that can decompose to generate free radicals and a second group comprises a radically transferable atom or group.

75. A alkyl(meth)acrylate macroinitiator formed by a low temperature atom transfer polymerization process with the initiator molecule of Claim 72, comprising a dihalosubstituted azo or peroxy compound to form a polyalkyl(meth)acrylate polymer initiator with an azo or peroxy group within the polymer chain which is suitable for use as an initiator for free radical polymerization of a vinyl acetate or vinyl chloride monomer at higher temperatures to form block copolymers.

76. A macroinitiator for a stable free radical mediated polymerization process, comprising the decomposition product of a process comprising decomposing the

macroinitiator of Claim 73 in the presence of an excess of a stable free radical.

77. The macroinitiator of Claim 76, which is formed by a low temperature controlled atom or group transfer polymerization of dimethylaminomethyl (meth)acrylate with an initiator comprising a dihalosubstituted group as an initiator for ATRP and a second functional group that will decompose to form free radicals, forming a polydimethylaminomethyl methacrylate macroinitiator containing said second functional group in the center of the polymer chain, for direct initiation of further free radically polymerizable monomers or conversion into an macroinitiator for a stable free radical mediated polymerization process by raising the temperature of the polymer to form a free radical in the presence of an excess of a stable free radical which reacts with the initially formed macro-free radical forming a thermally labile group suitable for further free radical mediated controlled free radical polymerization.

78. A macroinitiator for the preparation of block copolymers, comprising the reaction product of initiating a polymerization of a (co)monomer with the initiator of Claim 69, wherein the reaction product comprises one or more radically transferable atom(s) or group(s).

79. A macroinitiator of Claim 78, wherein the initiator of Claim 69 first polymerizes (co)monomers by a thermally initiated free radical process.

80. The macroinitiator of Claim 79, wherein at least one of styrene, vinyl acetate or vinyl chloride is initially polymerized by a thermally initiated free radical process and wherein the reaction product can prepare a block copolymer by polymerizing a second vinyl monomer selected from the group consisting of substituted styrene(s), (meth)acrylates, (meth)acrylonitriles, (meth)acrylamides and other monomers for ATRP.

81. An initiator for ATRP polymerization having the general formula:

$$Y\text{-}(X)_n \qquad (I)$$

wherein the core molecule Y comprises a small molecule or a macromolecule, a soluble or insoluble, organic, inorganic or composite molecule,

X is a radically transferable atom or group, and

n is the number of radically transferable atoms or groups on the core molecule.

82. The initiator of Claim 81, wherein Y comprises an organic molecule which comprise soluble, swellable, or insoluble molecules, a synthetic molecule or a natural-based material, crosslinked support or other organic materials initially containing one or more functional group(s) that are or can be substituted by known chemical processes to form group(s) containing one or more radically transferable atoms or groups.

83. The initiator of Claim 82, wherein the organic molecule comprises a synthetic molecule or natural-based material.

84. The initiator of Claim 83, wherein the natural-based material is selected from the group consisting of cellulose, glucose, cotton, wool, and derivatives thereof, and wherein the natural-based material is soluble or insoluble in a reaction media.

85. The initiator of Claim 82, wherein the organic molecule initially comprises at least one functional group selected from the group consisting of a hydroxy, thiol, amine, amide, and mixtures thereof.

86. The initiator of Claim 81, wherein Y is the biodegradation product of a biodegradable polymer.

87. The initiator of Claim 81, wherein Y may be fragmented in a recycling process for the recovery of reusable polymer segments.

88. The initiator of Claim 81, wherein Y may be degraded by moisture in a process for the preparation of repulpable polymers.

89. The initiator of Claim 81, further comprising an inorganic molecule or an inorganic surface which initially contains functional groups or derivatives thereof that contain one or more radically transferable atoms or groups or functional groups.

90. The initiator of Claim 81, wherein Y comprises a silica surface, a siloxane cube or a cyclotriphosphazene ring.

91. A macroinitiator for ATRP polymerization of free radically (co)polymerizable monomers, comprising a reaction product formed by a ring opening (co)polymerization of cyclic monomers or oligomers comprising a free radically transferable atom or group as a substituant.

92. The macroinitiator of Claim 91, wherein the ring opening (co)polymerization of cyclic monomers or oligomers is performed in the presence of a capping agent, and wherein the capping agent comprises a a radically transferable atom or group.

93. A polydimethylsiloxane macroinitiator prepared by the process of Claim 92.

94. A polyphosphazene multifunctional macroinitiator for an ATRP (co)polymerization, comprising the reaction product formed by a ring opening polymerization of cyclic hexachlorotriphosphazene followed by a reaction with a nucleophile containing radically transferable atoms of groups.

95. A polyphosphazene based functional polymeric macroinitiator for an ATRP (co)polymerization, comprising the reaction product of a ring opening polymerization of cyclic hexachlorotriphosphazene followed by a reaction with a nucleophile, wherein the nucleophile optionally contains radically transferable atoms or groups, and wherein the ratio

of nucleophiles that contain radically transferable atoms or groups to nucleophiles that do not contain radically transferable atoms or groups is from 99.9 to 0.1%.

96. A supported initiator for ATRP polymerization, formed by treating a surface with a molecule comprising a first functionality capable of reacting with said surface and a second functionality comprising one or more radically transferable atoms or groups.

97. The supported initiator of Claim 96, wherein the surface is an inorganic surface.

98. The supported initiator of Claim 96, wherein the surface is an organic surface.

99. A supported initiator of Claim 97, wherein the inorganic surface is a silica surface and the molecule comprises a substituted silane.

100. A macroinitiator for ATRP, comprising a reaction product of a polymerization in the presence of a transfer agent, wherein the transfer agent comprises a radically transferable atoms or groups.

101. A polyvinyl acetate macroinititor for ATRP, comprising a reaction product of a polymerization in the presence of a chain transfer agent, wherein the chain transfer agent comprises a radically transferable atom or group.

102. A macroinitiator for ATRP, comprising a reaction product of a living anionic polymerization, wherein the polymerization is quenched with a molecule comprising a radically transferable atom or group.

103. A macroinitiator for ATRP of free radically (co)polymerizable monomers, comprising a polystyrenic reaction product of conducting a living cationic polymerization and capping the resulting living cationic polymerization product by a styrene block comprising one or more styrene units, wherein the polystyrenic reaction product comprises a radically

transferable atom or group on a styrene termini.

104. A polyolefin (co)polymer macroinitiator, comprising a reaction product of reacting a polyolefin (co)polymer with at least one small molecule containing a radically transferable atom or group.

105. The polyolefin (co)polymer macroinitiator of Claim 104, wherein the small molecule is a halogen or a sulfonyl halide.

106. An initiator for the preparation of a "bottle brush" or comb shaped (co)polymer, comprising a reaction product of a linear polymerization of a monomer comprising a radically transferable atom or group, wherein the reaction product comprises an oligomer or polymer with a radically transferable atom of group residing on each monomer unit.

107. An initiator for the preparation of a "bottle brush" or comb shaped, or graft (co)polymers, comprising a reaction product of conducting a linear (co)polymerization of a monomer containing a radically transferable atom or group with a monomer that does not contain a functional group, wherein the reaction product comprises an oligomer or polymer with a known level of radically transferable atom of groups residing on the average polymer chain.

108. A multifunctional initiator for an ATRP polymerization to give a "bottle brush" or comb shaped (co)polymer, comprising a reaction product of a linear polymerization of a monomer containing a functional group, wherein the linear polymerization product comprises an oligomer or polymer comprising said functional group residing on each monomer unit and further reaction of said oligomer or polymer comprising said functional group with a compound containing a radically transferable atom or group, and wherein said

reaction product comprises a polymer with one or more radically transferable atoms or groups on each monomer unit.

109. A macromolecular initiator for the ATRP (co)polymerization to form graft or "bottle brush" copolymers, comprising a reaction product of reacting a mixture of compounds that contain a radically transferable atom or group and compounds that do not contain a radically transferable atom or group with the linear polymerization product of Claim 108, wherein said reaction product comprises a controlled number of radically transferable atoms or groups randomly distributed along the reaction product chain.

110. A multifunctional macroinitiator for preparation of a block copolymer with one or more "bottle brush" block(s), wherein at least one of the blocks in said block copolymer is prepared from a monomer containing a radically transferable group, or a group that can be converted to a group containing a radically transferable atom or group.

111. An initiator for a controlled polymerization process, which can be isolated or used in-situ, for the polymerization of free radically (co)polymerizable monomers, formed by the capture of a (functional)-free radical having the structure:

$$Z\text{-}I^* \qquad \text{(II)}$$

by reaction with a transition metal compound of the structure:

$$LMt^{n+1}Y_mX$$

wherein Z is any functional group, including non-reactive groups, that does not interact during an ATRP polymerization process,

Mt^{n+1} is a transition metal in the oxidation state n + 1,

wherein and X is a radically transferable counterion,

Y_m may be either the same as X, a radically transferable counterion different from X, or a

non-transferable counter ion, and

in the presence of solubilizing ligand(s) L,

wherein X is transferred from the metal compound to the free radical, creating a molecule of structure (III),

$$Z\text{-}I\text{-}X \qquad \text{(III)}$$

that can be isolated, or directly used as an initiator for controlled free radical (co)polymerization of monomers, optionally present in the system, through a catalyzed redox reaction with the metal compound now converted into a metal compound of lower oxidation state having the structure:

$$LMt^n Y_m \qquad \text{(IV)}$$

wherein Mt, X and Y are defined as above, and

I* is a substituted C, S, O, N, P, Sn, or any other atom that can form a free radical by any process.

112. The initiator Claim 111, wherein the said free radical is first formed by the decomposition of an organic peroxide, organic persulfate, inorganic persulfates, peroxydisulfate, azocompounds, peroxycarbonates, perborates, percarbonates, perchlorates, peracids, hydrogen peroxide, and mixtures thereof, optionally containing a functional group that does not interact in ATRP.

113. The process of Claim 111, wherein the transition metal complex is chosen to render the polymerization system homogeneous.

114. The process of Claim 111, wherein the monomers include substituted or unsubstituted acrylates, methacrylates, (meth)acrylamides and (meth)acrylonitriles.

115. The process of Claim 111, wherein one or more of the radically transferable